Shielding membrane surface carboxyl groups by covalent-binding graphene oxide to improve anti-fouling property and the simultaneous promotion of flux

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ABSTRACT

Graphene oxide (GO) is an excellent material for membrane surface modification. However, little is known about how and to what extent surface functional groups change after GO modification influence membrane anti-fouling properties. Carboxyl is an inherent functional group on polyamide or other similar membranes. Multivalent cations in wastewater secondary effluent can bridge with carboxyls on membrane surfaces and organic foulants, resulting in serious membrane fouling. In this study, carboxyls of a polydopamine (pDA)/1,3,5-benzenetricarbonyl trichloride (TMC) active layer are shielded by covalently-bound GO. The process is mediated by *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide (EDC)/*N*-hydroxysuccinimide (NHS). For GO containing low quantities of carboxyls, X-ray photoelectron spectroscopy (XPS) and zeta potential analyzer test results reveal that the carboxyl density decreased by 52.3% compare to the pDA/TMC membrane after GO modification. Fouling experiments shows that the flux only slightly declines in the GO functionalized membrane (19.0%), compared with the pDA/TMC membrane (36.0%) after fouling. In addition, during GO modification process the pDA/TMC active layer also become harder and thinner with the aid of EDC/NHS. So the pure water permeability increases from 56.3 ± 18.2 to 103.7 ± 12.0 LMH/MPa. Our results provide new insights for membrane modification work in water treatment and other related fields.

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1. Introduction

Membrane fouling limits the more widespread applications of nanofiltration (NF) or precise ultrafiltration (UF) membranes in water or wastewater treatment (Zhao and Yu, 2014). The membrane fouling caused by organic foulants in wastewater secondary effluent and some natural water is a difficult problem (Hong and Elimelech, 1997). For membranes surface with much carboxyls, the fouling process can be greatly enhanced by low concentrations of Ca^{2+} or other multivalent cations, because these cations can effectively coordinate with the carboxyls on the membrane surface

and organic foulants (Mo et al. 2011, 2012). As Ca^{2+} or other multivalent cations widely coexist with organic foulants in actual wastewater (Lu et al., 2013), reducing the carboxyls density on membrane surface can be a feasible choice to control this type of membrane fouling.

Carboxyl is an inherent group on polyamide (PA) membranes or other similar membranes, which can originate from the hydrolysis of unreacted acyl chloride groups during active layer preparation (Mo et al., 2012). Carboxyls can be the source of fixed charges in the membrane active layer after partial hydrolysis (Childress and Elimelech, 2000, 1996), and fixed charges have an important influence on the rejection efficiency of nanofiltration (NF) or similar precise ultrafiltration (UF) membranes (Szymczyk and Fievet, 2005). Above all, during the active layer formation, the excess numbers of acyl chloride groups may be favorable to the formation of three-dimensional active layer structures. The experiment

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described in previous work revealed the density of carboxyl groups could be decreased by selecting monomers with fewer acyl chloride groups to form the polyamide layer (Mo et al., 2012). But this method may also have an influence on the membrane divalent ion separation efficiency and flux (Mo et al., 2012). In addition, surface carboxyl groups can also be used for surface modification (Jie et al., 2015; Li et al., 2016; Yu et al., 2016).

Membrane active layer modification can improve membrane anti-fouling properties. The existing modification methods mainly include surface coating, surface grafting, incorporation of hydrophilic monomers/inorganic particles and zwitterionic modification (Zhao and Yu, 2014). However, in some cases, membrane flux, rejection efficiency, robustness and anti-fouling properties are mutually exclusive. Therefore, membrane modification methods may influence the water permeability (Lu et al., 2013; Van Wagner et al., 2011; Liu et al., 2015), surface roughness (Van Wagner et al., 2011), or rejection efficiency (An et al., 2011; Ye et al., 2015). Materials possessing better characteristics may help to handle these problems better.

Graphene oxide (GO) is an excellent material for membrane modification (Hegab and Zou, 2015). Water can nearly unimpeded permeated through graphene two-dimensional nanocapillaries (Nair et al., 2012). GO has other unique qualities, including ultra-high strength (Lee et al., 2008), atomic-scale thickness (Novoselov et al., 2004), high antibacterial property and low cytotoxicity (Hu et al., 2010; Tu et al., 2013), and the possibility of producing ultra-flat surface (Lui et al., 2009). It also possesses good chemical stability (Dreyer et al., 2010) and hydrophilic properties (Nair et al., 2012; Dreyer et al., 2010), and can be prepared from inexpensive graphite (Hu et al., 2010; Hummers and Offeman, 1958). Furthermore, there are abundant oxygen-containing functional groups on GO available for membrane modification. Several membrane surface modification reports have been published that use GO to improve flux (Chae et al., 2015; Berean et al., 2015), increase anti-biofouling properties (Hegab et al., 2015; Perreault et al., 2014; Zou et al., 2016) and enhance chlorine resistance properties (Choi et al., 2013). Previous studies also found that after surface modification by GO, the membrane anti-fouling properties to the protein, alginate or humic acid foulants were obviously improved (Hegab et al., 2015; Choi et al., 2013; Hu et al., 2016; Han et al., 2015). And the improvement of fouling resistance was attributed to hydrophilicity increase and surface roughness reducing (Hegab et al., 2015; Choi et al., 2013; Hu et al., 2016; Han et al., 2015). Even though GO have demonstrated effective adsorption performance (Perreault et al., 2015), it was explained that the organic foulants were adsorbed mainly on the basal plane of GO nanosheets while water enters in the GO modified membrane surface primarily around the oxidized edges of GO nanosheets (Hu et al., 2016). However, to the best of the authors' knowledge, there is little report on whether membrane surface functional groups change after GO surface modification influence membrane anti-fouling properties or not. A better understanding of these processes will help to the development of GO surface modification applications. Carboxyl group are present in low quantities at the periphery of moderately oxidized GO (Nair et al., 2012; Dreyer et al., 2010; Perreault et al., 2014). Here, we hypothesize that by covering carboxyls on the membrane active layer surface with GO nanosheets, Ca^{2+} bridged fouling could be significantly mitigated, whereas the rejection efficiency would not be affected because the volume charge density is maintained by protecting the carboxyls in the active layer using GO.

Novel polydopamine (pDA)/1,3,5-benzenetricarbonyl trichloride (TMC) composite membranes have the enormous potential for application in wastewater treatment and other fields (Zhao et al., 2014) because of their excellent structural and chemical stability (especially their chlorine resistance properties (Zhao et al.,

2014)). Dopamine can be easily self-deposited on nearly all types of inorganic and organic substrates with controllable thickness (Hu and Mi, 2013), and pDA has excellent durability (Liu et al., 2014). The amino and hydroxyl groups on the polydopamine can react with acyl chloride groups of TMC and other similar compounds to form amide bonds and ester bonds, constituting the active layer (Zhao et al., 2014; Hu and Mi, 2013; Liu et al., 2014). Thus, the pDA/TMC composite membrane is a good candidate membrane to investigate the relationship of how the surface carboxyl groups change affect the anti-fouling properties after surface modification by GO. As the pDA/TMC active layer could be low in roughness, high in hydrophilic properties (Zhao et al., 2014) the influence of these two aspects can be excluded easier. In addition, the controllable auto-polymerized membrane avoids uncontrolled errors during manually scraping membrane (Mo et al., 2012).

N-(3-Dimethylaminopropyl)-*N*'-ethylcarbodiimide (EDC)/*N*-hydroxysuccinimide (NHS) can be used to convert the native carboxyl groups of the polyamide surface into intermediate amine-reactive esters to covalently-bind GO or carbon nanotubes to membrane surface (Perreault et al., 2014; Tiraferri et al., 2011). EDC/NHS is also widely used to catalyze amide-crosslinks between carboxyl groups and amino groups (Wissink et al., 2001; Peng et al., 2013; Staros et al., 1986). The decline of membrane flux during the early stage of filtration is significantly affected by membrane compaction (Petersen, 1993). Thin-film composite (TFC) membrane compaction can occur in both the supporting layer and active layer. As the flux of the TFC membranes is controlled by the active layer (Petersen, 1993), Hussain et al. stated that the surface pore collapse may be the key mechanism for membrane compaction (Hussain et al., 2013). If EDC/NHS can enhance the amide-crosslinks between carboxyl groups and amino groups of pDA/TMC active layer, and suppress the surface pore collapse, the membrane flux can be promoted.

In this study, we use an environmentally friendly method to covalently-bind GO to the surface of pDA/TMC active layer, by EDC/NHS mediated interfacial polymerization to shield, but not remove, the carboxyls in the membrane active layer. We aim to simultaneously promote the anti-fouling property and flux, and maintain the membrane rejection efficiency.

2. Material and methods

2.1. GO preparation

GO was prepared from flaky graphite using the Hummers' method (Hummers and Offeman, 1958; Marcano et al., 2010). The high-temperature oxidation process at 98 °C was shortened to obtain moderately oxidized graphite oxide. The graphite oxide was washed using ultrapure water (Milli-Q) until the pH of the supernatant stabilized. Ultrasonic exfoliation (40 kHz, 100 W, Kun Shan Ultrasonic Instruments, China) of the GO nanosheets was performed in an ice bath for 1 h. The prepared GO solution was stored at 4 °C. Prior to use, the stock solution of GO was indirectly ultrasonicated for 10 min and diluted to the required concentration. The details of GO characterization methods and results (Figs. S1–S7) are listed in the Supplementary Information section.

2.2. Brief description of membrane fabrication

A new method was developed to prepare the GO functionalized pDA/TMC TFC membranes (Fig. 1). The main reactions and detailed description of the TFC membrane fabrication are provided in the Supplementary Information section. Briefly, a poly(vinylidene fluoride) (PVDF) microfiltration membrane (Shanghai SINAP Membrane Tech, Shanghai, China) with an average surface pore diameter of 80 nm was used as supporting membrane. The pDA/

TMC TFC membrane was fabricated by forming a pDA/TMC active layer on the surface of the PVDF membrane (known as pDA/TMC), followed by covalent-binding of GO on the active layer to obtain the GO functionalized pDA/TMC membrane (known as pDA/TMC/GO or PVDF/pDA/TMC/GO), using a method developed from previous reports (Perreault et al., 2014; Tiraferri et al., 2011). The layer-by-layer method was introduced to increase the amount of GO bound to the membrane surface (Sanyal and Lee, 2014). The rotation infusion Ethylenediamine (ED) and activated GO solutions were repeated 10 and 15 times to obtain multi-layer GO modified pDA/TMC membranes (known as pDA/TMC/GO10 or PVDF/pDA/TMC/GO10, pDA/TMC/GO15 or PVDF/pDA/TMC/GO15).

To confirm the effectiveness of the GO modification method and obtain a clearer scanning electron microscope (SEM) image, a polyethersulfone (PES) microfiltration membrane (HangZhou DUTE Filter Company, China) was also used as the supporting membrane, with the same method described above (known as PES/pDA/TMC/GO10) to prepare the GO modification membrane. The PES microfiltration membrane possesses a larger pore size (in general 0.5–2 μm) than the PVDF supporting membrane, so the pDA/TMC active layer cannot coated on the micropores of PES supporting membrane well, and GO nanosheets were easier to be distinguished using SEM.

pDA/TMC/C10 membranes were measured at a resolution of 4 cm^{-1} and excitation wavelength of 532 nm. Au colloid (Sun et al., 2014) was dropwise added to the membrane samples and dried at $45\text{ }^{\circ}\text{C}$ to make up the surface-enhanced Raman scattering (SERS) to enhance the spectra signals.

The surface functional groups of the dried membranes were determined using X-ray photoelectron spectroscopy (XPS, Thermo Scientific Escalab 250Xi, UK) using 300 W of Al K α radiation at approximately 3×10^{-9} mbar. The bond energies were referenced to the C1s line at 284.8 eV from adventitious carbon and the $-\text{C}-\text{F}$ line at 290.35 eV from the PVDF supporting membrane. After the C1s peak of the membrane was deconvoluted, the area percentages of the functional groups in the active skin layer were calculated. To obtain a more accurate result, the carbon atoms in the supporting layer were removed. The chemical formula of PVDF supporting layer is $-(\text{CH}_2-\text{CF}_2)_n-$. So when there was a unit of $-\text{C}-\text{F}$ peak area showed in XPS C1s peak, there was a unit of $-\text{C}-\text{C}-$ peak area belonged to PVDF supporting layer also showed accompanying. Therefore, there was twice as many carbon atoms in the PVDF supporting layer should be subtracted compared with the $-\text{C}-\text{F}$ area percentages. For example, the carboxyl area percentage in the pDA/TMC active skin layer was calculated as

$$\text{Area percentage}(\text{COOH}) = \frac{\text{Area}(\text{COOH})}{\text{Area}((\text{C}-\text{C}/\text{C}=\text{C}) + (\text{C}-\text{N}) + (\text{C}=\text{O}) + (\text{C}-\text{O}-\text{C}/\text{C}-\text{OH}) + (\text{COOH}) + (\text{C}-\text{F})) - 2\text{Area}(\text{C}-\text{F})} \times 100\% \quad (1)$$

To elucidate the impact of the GO modification and EDC/NHS catalyst on the anti-fouling and filtration properties of the membrane, control membranes without a GO layer (known as pDA/TMC/C10 or PVDF/pDA/TMC/C10) were fabricated following the same procedure mentioned above, with the exception of replacing the GO solution with ultrapure water.

2.3. Membrane characterization

The microstructure of membrane surfaces was observed using a field emission scanning electron microscope (FESEM, Hitachi SU8020, Japan). The samples were dried in an oven at $45\text{ }^{\circ}\text{C}$ and sprayed with Au for 10 s under fine vacuum conditions, prior to observation. The Raman spectra (LabRam HR Evolution of Hoeiba Jobin Yvon, France) of the pDA/TMC/GO10, pDA/TMC/GO15 and

The zeta potential of the membrane surfaces was determined using a SurPASS electrokinetic analyzer with an adjustable gap cell (cell height of $100 \pm 10\text{ }\mu\text{m}$, Anton Paar GmbH, Austria) (Buksek et al., 2010). Measurements were carried out in a 1 mM KCl solution at $25 \pm 1\text{ }^{\circ}\text{C}$. The pH was set in the range of 4–10 by adding HCl or KOH. Prior to the measurement, the samples were equilibrated with the testing solution for at least 45 min (Ben-Sasson et al., 2014). The original Helmholtz-Smoluchowski approach was applied to calculate the zeta potential (Buksek et al., 2010).

To get the cross section view of membrane active layer, the cross-sectional transmission electron microscope (TEM) images of different membranes were taken using ultramicrotomy. The samples for ultramicrotomy were firstly embedded in Eponate resin and solidified for 48 h at $60\text{ }^{\circ}\text{C}$. The embedded samples were sliced to pieces with the thickness of $\sim 70\text{ nm}$ by an ultramicrotome

Fig. 1. The main procedure to prepare GO functionalized membranes.

(Ultracut UCT, Leica Microsystems IR GmbH, Germany) and observed by an TEM (JEM-1400 from JEOL Ltd.) at 80 kV.

2.4. Membrane compaction and rejection performance test

The membrane compaction process, water permeability, rejection performance were tested on a modified SEPA CF II membrane cell system (Sterlitech Corporation, USA) with an effective membrane area of 137.1 cm². All of these tests were conducted at a transmembrane pressure (TMP) of 0.45 MPa and a cross-flow velocity of 0.132 m/s. The temperature of the feed solution was 26 ± 1 °C. Ultrapure water was used for membrane compaction and water permeability measurement. The flux before a certain time was manually recorded to represent the compaction process. When flux change was stable, the water permeability, A_k , was then calculated as:

$$A_k = \frac{\Delta V}{A_m \Delta P \Delta t} \quad (2)$$

Where, A_m is the effective membrane surface area, ΔV is the collected permeate volume during Δt , and ΔP is transmembrane pressure (TMP).

Rejection performance was characterized by solutions of Alizarin red S (10 mg/L), chromotropic acid disodium (10 mg/L) and Rhodamine B (10 mg/L) with the pH adjusted to 7.0. The concentrations of the Alizarin red S, chromotropic acid disodium salt and Rhodamine B were measured using a spectrophotometric method with a Beckman Coulter DU730 spectrophotometer (Beckman Coulter, Inc, USA) at wavelengths of 261, 233 and 553 nm, respectively. The apparent rejection to organic matter, R , was calculated from:

$$R = 100\% \times \left(1 - \frac{C_p}{C_f}\right) \quad (3)$$

Where, C_p and C_f are the concentrations of tested organic matter in the permeated and feed solutions, respectively.

2.5. Anti-fouling property test

Membrane fouling testing was performed in the same modified SEPA CF II membrane cell system mentioned in Section 2.4 using a previously reported process (Mo et al., 2012; Choi et al., 2013; Han et al., 2015). The Ca²⁺/organic foulants compound synthetic wastewater was constituted by CaCl₂, NaCl, NaHCO₃ and sodium alginate (Mo et al., 2012; Lu et al., 2013). Before fouling, the compacted membranes were equilibrated with a background electrolyte containing 1 mM CaCl₂, 16 mM NaCl and 1 mM NaHCO₃ (Mo et al., 2012) until the flux stabilized. The cross-flow velocity during this stage was 0.11 m/s. The same TMP of 0.45 MPa was chosen to exclude the impact of TMP on membrane fouling (Xie et al., 2015). Alginate was used as a model macromolecule for the fouling experiment. Sodium alginate solution was added to the background solution to achieve an alginate concentration of 20 mg/L to initialize the fouling stage. The fouling experiment was performed until the filtrate was more than 600 ml. Physical cleaning was performed to evaluate fouling reversibility. The cross-flow velocity was increased to 0.44 m/s, and the hydraulic pressure was kept close to zero. The composition of the cleaning solution was same as the background electrolyte. After 30 min of physical cleaning, the same background electrolyte was used again to determine the flux of a cleaned membrane. The cleaning efficiency was calculated as previous reports (Mo et al., 2012).

3. Results and discussion

3.1. Physicochemical properties of GO

Single-layer GO nanosheets were successfully prepared at thicknesses ranging from 0.8 to 1.1 nm (Fig. S1), and the plane size of GO was approximately 1–6 μm (Fig. S2). As GO nanosheets tend to be planar superimposed when concentration reach to a certain level, they can only be recognized by wrinkles in the FESEM image (Fig. S3). The Raman spectra exhibited characteristic D peaks at ~1350 cm⁻¹, which are associated with the order/disorder of the system, and G peaks at ~1590 cm⁻¹, which are an indicator of the stacking structure (Dreyer et al., 2010; Das et al., 2008) (Fig. S4). The zeta potential measurement revealed that the GO nanosheets were negatively charged (< -60 mV) and stably dispersed in the water over a wide pH range of 4–10 (Fig. S5) (Riddick, 1968). This negative potential likely originated from the selective adsorption of OH⁻ or Cl⁻ on GO rather than the hydrolysis of the carboxyl, as the zeta potential did not become more negatively charged with the increase in pH (Fig. S5).

XPS spectra and Fourier transform infrared spectroscopy (FTIR) spectrum (Fig. S6) of GO (Fig. S7, Table S1) were also obtained. After deconvolution of the XPS data (Table S1), the obtained GO nanosheets were found to be abundant in -C-OH/-C-O-C (aromatic) groups (42.9%). The -COOH area percentage in each side of the GO nanosheets was only 1.2%. This revealed the tremendous potential of using GO to shield membrane surface carboxyls.

3.2. Formation of pDA/TMC active layer

As revealed by FESEM, the surface of the pDA/TMC TFC membrane (Fig. 2b) was basically with no micropore, different from the pristine PVDF membrane (Fig. 2a), indicating that the pDA/TMC active layer formed after the dopamine and TMC treatment (Fig. 2g–i). At the same time, the water permeability decreased sharply from 5487.8 ± 398.5 L/(m²·h·MPa) to 56.3 ± 18.2 L/(m²·h·MPa) (Fig. 5a). The pDA/TMC active layer formation was further supported by the ATR-FTIR differential spectra (Fig. S12), which showed that an amide peak emerged at approximately 1720 cm⁻¹ (Zhao et al., 2014), after reacting with TMC.

3.3. Irreversible binding of GO

The GO characteristic peaks (G peaks at ~1590 cm⁻¹ and D peaks at ~1350 cm⁻¹) were captured in the Raman spectra (Fig. 3) after GO functionalization. Moreover, the intensities of the G and D peaks increased by 50%, coupling with the GO functionalization times increased from 10 to 15. Furthermore, GO characteristic folds also emerged on the surface of the membrane after GO functionalization (Fig. 2c). Clearer GO images (Fig. 2e, f) were also obtained when the PES microfiltration membrane with larger pore sizes (0.5–2 μm) was used as the supporting membrane to prepare GO functionalized membranes. The FESEM images and Raman spectra confirmed the effectiveness of the GO functionalization method.

3.4. Membrane surface carboxyl shielding

The functional group ratios of GO, pDA/TMC and pDA/TMC/C10 membrane active layers are listed in Table S1 and Fig. 4a–d after C1s peak was deconvoluted and calculated. As shown in Fig. 4a–d and Table S1, the average -COOH density in the pDA/TMC/GO layer decreased from 4.4% to 2.1% compared with the pDA/TMC active layer in the pDA/TMC membrane. Furthermore, from the Table S1 and Fig. 4b–d, we can also find that during GO functionalization process, the covalent-binding GO on the membrane surface was

Fig. 2. FESEM and TEM images of different membranes: (a) Pristine PVDF microfiltration membranes. (b) Polydopamine/TMC on the PVDF supporting membrane (known as PVDF/pDA/TMC). (c) Membrane functionalization by GO (known as PVDF/pDA/TMC/GO10), (d) pristine PES microfiltration membranes. (e, f) GO functionalized PES microfiltration membranes (known as PES/pDA/TMC/GO10). (g, h, i) Cross-sectional TEM view of different membranes. PVDF/pDA/TMC/C10 means the control membrane of PVDF/pDA/TMC/GO10 without GO addition.

mainly aided by the $-C-N-$ bonds that formed from the ED and epoxy of the GO (Hung et al., 2014) (see the discussion in Supplementary Information). However, a small amount of $-COOH$ also formed to amide bond with the ED aided by EDC/NHS (Perreault et al., 2014). Therefore, the remaining $-COOH$ on one side of the GO could be less than 1.2%. In addition, GO nanosheets are a two-dimensional material, and the carboxyls tend to be homogeneously distributed on the two side of the nanosheets. As the XPS data only revealed the average value of $-COOH$ density at a certain depth, not at the outer surface of the pDA/TMC/GO layer. Therefore, the reality $-COOH$ density in the outer surface could be less than 2.1%.

Zeta potential analyzer results also revealed membrane surface $-COOH$ shielded by the GO (Fig. 4e). Compared with the relative stable zeta potential of the pDA membrane containing no $-COOH$, all of the $-COOH$ -containing membranes (pDA/TMC, pDA/TMC/C10 and pDA/TMC/GO10) become more negatively charged in their zeta potential along with the increase in pH. This demonstrated that the dissociation of $-COOH$ ($pK_a \approx 3.5$, predicted by ACD/Labs) on the membrane surface was the main contributor to the change

in the surface zeta potential, so the zeta potential can be an indicator of the $-COOH$ density on the membrane surface (Childress and Elimelech, 2000, 1996). The zeta potential of the pDA/TMC (-54.1 mV) and the pDA/TMC/C10 (-53.5 mV) membranes were both considerably more negatively charged than that of the pDA/TMC/GO10 membrane (-45.1 mV) at pH 7, which provided further evidence that the $-COOH$ on the membrane surface was effectively shielded by the GO during the membrane modification.

The GO nanosheets were expected to shield only the outer surface of the pDA/TMC active layer, meaning that the carboxyls under the GO layer could still contribute to the volume charge density of the active layer after partial hydrolysis (Childress and Elimelech, 2000, 1996). The volume charge density had an important effect on the rejection efficiency of nanofiltration (Szymczyk and Fievet, 2005) and was not easy to be tested. However, this effect can be indirectly discussed using the rejection efficiency results.

The membrane rejection efficiency to carefully select organics could reveal the volume charge density of the active layer. The rejection efficiencies of pDA/TMC/GO10 and pDA/TMC/C10 for

Fig. 3. Raman spectra recorded from the pDA/TMC/GO membranes and the control membrane.

chromotropic acid disodium (with two negative charges at pH 7) were $90.5 \pm 2.5\%$ and $87.3 \pm 4.2\%$, respectively, and the rejection efficiencies were $81.6 \pm 0.4\%$ and $81.8 \pm 0.8\%$ for Alizarin Red S (with one negative charge at pH 7), respectively. For Rhodamine B (an apparent positive charge at pH 7), the apparent rejection efficiencies of pDA/TMC/GO10 and pDA/TMC/C10 were $11.4 \pm 6.4\%$ and $4.5 \pm 1.1\%$, respectively. The ionic weights of chromotropic acid disodium, Alizarin Red S and Rhodamine B were 318.28, 319.27 and 443.51, respectively. Therefore, the number of negative charges directly affected the level of apparent rejection efficiency, and the role of ionic weights was limited to the rejection for these three organic compounds. The apparent rejection efficiency also revealed that the effective pore size of the membrane active layers in this study was larger than Stokes' radius for the Rhodamine B ion. Furthermore, there was a high volume charge density in the active layers according to the Donnan-Steric partitioning pore model (Szymczyk and Fievet, 2005; Bowen and Mukhtar, 1996; Vezzani and Bandini, 2002). Therefore, the apparent rejection efficiency remains constant after the GO functionalization revealed that the volume charge density remains constant. This means that after carboxyls in the active layer were shielded by the GO, the carboxyls beneath the GO nanosheets could still provide a fixed charge and contribute to the higher volume charge density formation.

3.5. Anti-fouling property enhancement

Fouling tests were conducted on the pDA/TMC, pDA/TMC/GO10 and pDA/TMC/C10 membranes with synthetic wastewater containing Ca^{2+} /organic compound foulants, as organic foulants and calcium ions often coexist in wastewater secondary effluent or some natural water (Lu et al., 2013). Calcium and other multivalent cations have been reported to accelerate the fouling process by 'bridge' between the carboxyl groups of the polyamide membrane surface and alginate (Mo et al. 2011, 2012). The pDA/TMC/GO10 membrane exhibited a slower normalized flux decline than the pDA/TMC and pDA/TMC/C10 membranes (Fig. 6). At the end of the fouling tests, the normalized flux of the pDA/TMC/GO10 membrane decreased by 19.0%, which is considerably less than those from the pDA/TMC (36.0%) and pDA/TMC/C10 (48.8%) membranes. These results suggest that the membranes became more resistant to fouling after the covalent-binding of the GO to the membrane surface. The fouling reversibility of the GO functionalized membrane (18.0%) was also higher than those of the pDA/TMC and pDA/

TMC/C10 membranes (<1%). Hence, the anti-fouling property of the membranes were clearly enhanced after GO shielding.

Membrane characteristics that can influence the anti-fouling properties typically include surface roughness, wettability, surface charge and surface functional groups (Mo et al., 2012; Hobbs et al., 2006; Ni et al., 2014; Wu et al., 2014; Vrijenhoek et al., 2001). The surface roughness and water contact angles of the pDA/TMC membrane were already relatively low. Therefore, the roughness of the membrane surface does not exhibit significant changes after GO functionalization compared with the pDA/TMC membrane (P-Value>0.05, Fig. S13), and the water contact angles change of GO modified membranes were also insignificant (P-Value = 0.197 > 0.05) (Fig. S14). These results indicate that compared with the pDA/TMC membrane, the enhanced anti-fouling property of the GO functionalized membrane in this study do not originate from changes in the surface roughness and wettability. For the surface charge, it has been suggested that a more negatively charged membrane zeta potential may lead to greater repulsion to negatively charged foulants (Mo et al., 2012). The sodium alginate was negatively charged (Contreras et al., 2011). However, because the GO functionalization membrane's zeta potential was more positively charged (Fig. 4e), the repulsion became lower. It meant that the surface charge change could not be the reason for the enhancement of the membrane anti-fouling properties. Moreover, the membrane zeta potential difference will be compressed to minimum by Ca^{2+} or other multivalent cations and can be ignored (Mo et al., 2012). For the surface functional groups, previous findings indicate that membranes with more $-\text{COOH}$ surface groups attract more alginate in the initial conditioning layer than other groups (Wu et al., 2014). After carboxyls were shielded by the GO nanosheets (Fig. 4), the calcium bridging between the carboxyl groups of alginate molecules and those of the membrane surface were weakened. Therefore, compared with the pDA/TMC membrane, fewer carboxyls appear on the membrane surface after shielded by GO was the most likely reason for the enhancement of anti-fouling properties.

3.6. Reasons for the increase in water permeability

As in Figs. 5a and 7 showed that the water permeability of the GO functionalized membrane (pDA/TMC/GO10) ($103.69 \pm 12.04 \text{ L}/(\text{m}^2 \cdot \text{h} \cdot \text{MPa})$) increased by 84.2% compared with that of the pDA/TMC membrane ($56.28 \pm 18.18 \text{ L}/(\text{m}^2 \cdot \text{h} \cdot \text{MPa})$). However, this increase in water permeability cannot be attributed to the GO functionalization because the water permeability of the control membrane (pDA/TMC/C10) also increased (Figs. 5a and 7). The reason for increase in water permeability was membrane active layer becoming harder and thinner after the EDC/NHS catalyzed.

EDC/NHS is widely used to catalyze amide-crosslinks between carboxyl groups and amino groups (Wissink et al., 2001). Fig. 4b, c and Table S1 illustrated that the $-\text{C}-\text{N}-$ and $-\text{C}(=\text{O})-\text{NH}-$ peaks of pDA/TMC/C10 membrane increased after catalyzed by the EDC/NHS compared with the pDA/TMC membrane. The $-\text{COOH}$ decrease agreed with $-\text{C}(=\text{O})-\text{NH}-$ increase well ($\sim 0.9\%$ for both, Table S1). These results indicate that a small proportion of the $-\text{COOH}$ on the pDA/TMC active layer formed to amide bonds. The more amide-crosslinks formed made membrane active layer becoming harder, which can be supported by the results from the membrane compaction tests (Fig. 7 and S11). The active layer surface pore collapse is one of the key mechanisms for membrane compaction (Hussain et al., 2013). As the compaction tests (Fig. 7 and S11) showed, membranes water permeability all sharply decreased at the beginning of the test, indicating that the membranes were compacted rapidly. However, the stable fluxes of the pDA/TMC/C10 and pDA/TMC/GO10 were notably higher than that

Fig. 4. (a) Carboxyl area percentage in the pDA/TMC active layer, pDA/TMC/GO layer and GO nanosheets calculated from the XPS spectra C1s peaks data. (b), (c) and (d) XPS spectra C1s peaks for different membranes. (e) Membrane surface charge represented by zeta potential ($n = 4$). The pDA means that the PVDF membrane was treated using dopamine only.

of pDA/TMC membrane. These results revealed the formation of a harder pDA/TMC active layer after catalyzed by the EDC/NHS.

The $-\text{C}-\text{F}$ peak increased after the EDC/NHS treatment based on the XPS C1s data (Fig. 4b, c and S10), which could indicate the pDA/TMC layer became thinner. The $-\text{C}-\text{F}$ peak could only originate from PVDF supporting layer. For the same X-ray excitation energy,

the ability of the excited state electron in the PVDF layer to escape away from the membrane surface is related to the thickness of the pDA/TMC layer above the PVDF layer (Karan et al., 2015). The $-\text{C}-\text{F}$ peak increase meant more excited state electrons belonging to the PVDF layer escaped from the membrane surface. That revealed a thinner pDA/TMC layer formed.

Fig. 5. (a) Water permeability of different membranes ($n = 3$) and (b) apparent rejection data for different membranes to different organic compounds.

Fig. 6. Anti-fouling property to Ca^{2+} and alginate compound fouling. J_0 is the stable flux prior to the fouling stage, and J is the real-time flux during the tests. The anti-fouling property tests were performed with an electrolyte solution containing 1 mM CaCl_2 , 16 mM NaCl , 1 mM NaHCO_3 and 20 mg/L sodium alginate. The cross membrane pressure was 0.45 MPa with a cross-flow rate of 0.11 m/s.

Fig. 7. Water permeability change for different membranes in the early compaction stage. All of the membrane compaction tests were performed under 0.45 MPa with a cross-flow rate of 0.132 m/s.

The cross-sectional TEM views of different membranes (Fig. 2g–h) gave direct evidence that pDA/TMC layer became thinner. The thickness of pDA/TMC active layer decreased from 8.9–19.6 nm to 7.2–12.7 nm after EDC/NHS treatment.

As the membrane active layer becomes harder and thinner, the surface density of nanopores increased and the collapse of nanopores was eased, thus the water flow path became shorter. All of these resulted in an increase in membrane water permeability.

3.7. Importance of active layer carboxyls shielding and simultaneous promotion of flux along with anti-fouling property

The special features of the GO (Hegab and Zou, 2015; Nair et al., 2012; Lee et al., 2008; Hu et al., 2010; Tu et al., 2013; Lui et al., 2009; Novoselov et al., 2004; Dreyer et al., 2010; Hummers and Offeman, 1958; Drili et al., 2015) make it to an excellent surface modification material. The GO surface modification can effectively exert the good separation properties of organic polymer active layer, and the chlorine resistance and anti-fouling properties of a GO layer simultaneously. A profound understanding of the relationship between the membrane surface functional groups change and the anti-fouling properties change after the GO surface modification is important to the development of GO surface modification. In this work, we proved that by shielding, but not removing the carboxyl groups on the membrane active layer using GO led to improvements in the membrane anti-fouling property. These results are important to multivalent cations/organic foulants compound fouling control, during the membrane purification of natural water and wastewater secondary effluent. Future studies could focus on preparation and selection of GO with different properties, and use them for different modifications purposes.

People are continuously working on pursuing membranes with higher flux. However, higher water permeability means a higher concentration polarization effect for the same operating conditions (Cohen-Tanugi et al., 2014), implying more serious membrane fouling (Bacchin et al., 2006). Our fouling tests (Fig. 6) revealed that flux decline rate of the flux-improved membrane (pDA/TMC/C10) was faster than that for the low flux membrane (pDA/TMC) because the concentration polarization effect increased. This effect significantly offset the amount of flux increment. However, when we promote the flux along with anti-fouling property (pDA/TMC/GO10), the flux after fouling is clearly increased, although the concentration polarization effect also increased compared with the low-flux membrane (pDA/TMC). These results reveal the importance of increasing membrane flux and anti-fouling properties

simultaneously, from a practical application perspective.

4. Conclusions

In this work, GO nanosheets were covalently-bound to the surface of a polydopamine/TMC membrane using an environmentally friendly, layer-by-layer self-assembly method, aided by EDC/NHS-mediated interfacial polymerization. We found that the high increase of membrane anti-fouling properties after GO modification can also result from shielding active layer carboxyl groups by GO nanosheets, apart from previously reported increase in hydrophilicity and reduction in membrane surface roughness. The GO covalently-binding method we used effectually protected the volume charge density of active layer, so the membrane rejection efficiency maintained relatively stable. The EDC/NHS catalysis made the active layer of polydopamine/TMC membrane became thinner and harder by enhancing the amide-crosslinks between carboxylic and amino groups. Membrane flux obviously increased along with GO covalent-binding process.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.watres.2016.06.032>.

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